gasoline vehicles, urban soil, coal soot, biogenetic–derived secondary organic aerosol and toluene–derived secondary organic aerosol.

Anhydrosugars and sugar alcohols (carbonaceous species) are photo-chemically less reactive comparison to the other biomarkers for biomass burning (Simoneit, 2002) so persisting in the atmosphere for a long time. Anhydrosugars and sugar alcohols are complex materials composed of distinct types of cells of plants which change during the growing season (Hoffer *et al*., 2006). Anhydrosugars and sugar alcohols are the products of thermal degradation of cellulose and hemicelluloses; they are the major constructive part of plants therefore analysis of sugar alcohols (Xylose, fructose, mannose, galactose, glucose, sucrose, trehalose, glycerol, threitol, erythritol, arabitol, mannitol and inositol) and anhydrosugars (Levoglucosan, galactosan, mannosan, arabinosan, N–acetyle–2–amnoglucosan and 1,6–anhydroglucofuranose) (Kundu *et al*., 2010) in atmospheric aerosols is important (Mochida and Kawamura, 2004). Among the tracer for biomass burning; the levoglucosan, mannosan and galactosan are known as key marker for biomass burning (Lee *et al*., 2010; Stone *et al.,* 2011).

The observed high percentage of these compound indicates that the smoke is originated from biomass burning such as coal, rice straw, wheat straw, cow dung cake and wood (Sheesley *et al*., 2003; Alves *et al*., 2011). Herrmann and coworkers, (2010) performed the detailed kinetic study on the reactivity between levoglucosan and OH^-, NO_3^- or SO_4^{2-} ions in aqueous solution, and the result bare that OH^- is leading oxidant. Relative kinetics indicates that levoglucosan has an atmospheric lifetime of 0.2–2.2 days when biomass burning particles are exposed to 1×10^6 molecules cm^{-3} of OH^- (typically averages summertime conditions), this implies that levoglucosan reacts with OH^- on a timescale similar to that of transport and deposition, which has important implication for the use of levoglucosan as tracer for biomass burning emission in source apportionment studies (Hennigan *et al*., 2010), therefore, the levoglucosan is widely known as the organic tracer for biomass burning, including specific marker for wood burning (Zdrahal *et al*., 2002; Simoneit *et al.*, 2004; Fabbri *et al*., 2009). In addition, non-mineral potassium is also known as marker for wood burning in the atmosphere but there are many other sources (sea salt) for potassium apart from the wood burning (Sang *et al*., 2010).

3. A brief review on the work has been already down in this field

3.1 Anhydrosugars and sugar alcohols in world climate

According to Sheesley and Schauer (2003) the concentrations were ranged from 18.3 to 98.4 µg/mg for levoglucosan, 0.73 to 2.80 galactosan and 0.44 to 1.35 µg/mg mannosan and average high concentration of anhydrosugars were obtained for biomass briquettes while low for rice straw over South Asia. In a case study of a Quercus and Picea mixed forest in Hokkaido, (Japan) the concentrations were ranged from 1.1−7.5 fructose, 9.8−32 glucose, 0.2−13 sucrose, 1.5−8.4 trehalose, 3.7−25 glycerol, 4.9−30 arabitol, 6.9−21 mannitol, 0.1−1.3 inositol, and 28−93 ng/m^3 subtotal for the sampling year of 2001 (Fu and Kawamura, 2011). Over Rondonia, Brazil for year of 2002, the concentrations of anhydrosugars were higher during dry period compared to transition and wet period (Kourtchev *et al*., 2010). According to Kundu *et al*. (2010) for the year of 2002, the concentration of levoglucosan ranged between 850−7310 ng/m^3 (Average 2550 ng/m^3) in daytime while at nighttime it was 2510−8790 ng/m^3 (Average 5650 ng/m^3) and same pattern followed by its stereo isomer, in Rondonia, Brazil. In Rondonio, Brazil, (2002) among the anhydrosugars analyzed levoglucosan was the dominant species (850−7310 ng/m^3) and in sugar alcohols erythritol was dominant species (22.1−44.9 ng/m^3) (Kundu *et al*., 2010).

In $PM_{2.5}$ aerosol sample for the year of 2002 and 2004, over five rural sites in Europe the levoglucosan concentration varied from 2.7 to 1220 in winter time and 4.5 to 10.4 ng/m^3 in summer time, i.e., more concentration was found during winter time. Maximum concentrations of levoglucosan in aerosol samples ($PM_{2.5}$) were found to be 91.5 (Average−30, 48 hour sampling time) and 133.7 (Average−36.0, 24 hour sampling time) ng/m^3 at rural and urban sites, respectively for the year 2004 in southeast China (Sang *et al*., 2011). In a case study by Stone et al. (2011) the average levoglucosan concentration was higher in $PM_{2.5}$ (8.64 ng/m^3) rather than in $PM_{2.5-10}$ (4.70 ng/m^3) in Gosan, Korea, for year of 2007. By the controlled field burning of rice straw, the concentration of levoglucosan in $PM_{2.5}$ was higher (Average 1582 ng/m^3) compared to $PM_{2.5-10}$ (Average−107 ng/m^3) in rural part of Yunlin country, Taiwan for the year of 2007 (Engling *et al*., 2009). As expected, the levoglucosan was the most abundant anhydrosugars, followed by the mannosan and galactosan, these particle were detected in fine particles at an average levels of 13.9, 8.40 and 6.21 mg/g organic carbon (OC), while in coarse particles the

average values were 9.65, 5.65 and 4.23 mg/g OC, respectively in Penedono, central Portugal for the year of 2009 (Vicente *et al*., 2011).

3.*2 Concentration of anhydrosugars and sugar alcohols in India*

India has been facing serious problem regarding the PM pollution due to rapid industrialization and economic growth. The major source in indo–Asian haze is due to significant industrial emission, biomass burning, coal burning and vehicle exhaust (Fu *et al*., 2009). Perrino and his coworker (2011) reported that the concentration of levoglucosan ranges from 0.50–3.0 (average 1.7) for 2009, 0.15–0.57 (0.41) $\mu g/m^3$ for 2010 in PM_{10} over New Delhi, India.

4. Present investigation

Anhydrosugars and sugar alcohols related degradation product from the cellulose and hemicelluloses can be utilized as specific and general indicator compound for the presence of emission from biomass burning in the sample of atmospheric PM. Anhydrosugars and sugar alcohols that emits in large amounts, are sufficiently stable and are specific to burning and hemicelluloses containing substances. Thus it meets all important criteria to serve as an ideal molecular of biomass burning. Previous investigation of anhydrosugars and sugar alcohols in smoke aerosols derived from agriculture residue, domestic and biomass burning activities are limited to several ambient studies. However, none of previous studies included the measurement of anhydrosugars and sugar alcohols as tracers for biomass burning in India. The major objective of this study will be therefore to determine the PM concentration and size distribution of selected molecular tracer (Anhydrosugars and sugar alcohols) for biomass burning over the full size spectrum and to specially investigate the composition of anhydrosugars and sugar alcohols constituent in the smoke aerosol. The main objective of this study will be to determine the concentration of PM associated with anhydrosugars and sugar alcohols in collected aerosol sample of rural and urban area in central India.

Objectives of work

1. To study the size and mass distribution of atmospheric particles and associated anhydrosugars and sugar alcohols with seasonal distribution in the urban and rural area of central India.
2. To study the mass levels of anhydrosugars and sugar alcohols in PM_{10}, $PM_{2.5-10}$, $PM_{2.5}$ and PM_1 particles in the urban and rural site of central India.
3. To study the role of climatic parameters on the distribution of size-differentiated atmospheric particles in the urban and rural site of central India.
4. To study the relationship between size-segregated aerosol and associated anhydrosugars and sugar alcohols employing correlation and principal component analysis.
5. To study the spatial variation of size-segregated particulates and associated anhydrosugars and sugar alcohols in urban and rural site of central India.

5. Noteworthy contribution in the field of proposed work:

In our laboratory reasonable amount of work related to the monitoring, sampling and analysis of metallic pollutants, including arsenic in various kind of sample like, airborne dust particulates, soil, sediments and water have been carried out. A substantial amount of work on the diversified topics related to the environmental chemistry like study on dust fall-out in urban city of Chhattisgarh have been carried out (Deb *et al*., 1998; Deb and Thakur, 1999). High concentration of heavy metals such as As, Sb, Pb, Fe, Cu, Zn, Ni, Co & Mn were reported in the dust fall-out of the premiere and capital city of Chhattisgarh (Thakur and Deb, 2000). Sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) determination have been carried out in ambient air with diffuse reflectance fourier transform infrared spectroscopy (Verma *et al.*, 2007; Verma and Deb, 2008). Sulphate and nitrate were determined in aerosol samples with diffuse reflectance Fourier transform infrared spectroscopy using KBr substrate (Verma and Deb 2007a, b). Determinations of water−soluble inorganic ions have been done in the Durg and Raipur city of Chhattisgarh (Deshmukh *et al.*, 2012). PM load estimation in the urban area of Chhattisgarh has been successfully done. PM concentration and size distribution of water-soluble dicarboxylate species and major inorganic ions in aerosol sample have been characterized by ion chromatography (Deshmukh *et al.*, 2012).

6. Proposed methodology during the tenure of the research work:

To achieve the goal following approaches will be considered

A. Study area

The ambient aerosol samples will be collected in the urban and rural site of central region of India.

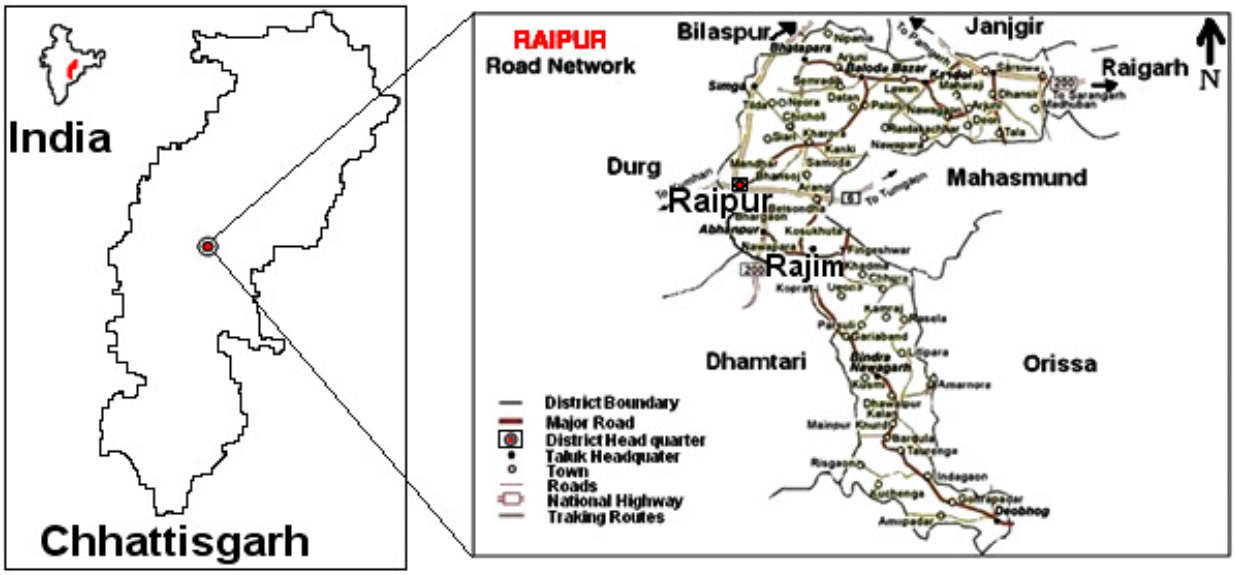


Fig. 12 Map of sampling locations at urban and rural areas.

1. *Urban area (Raipur)*

The aerosol collection will be performed at about 15 meter above the ground level at Pt. Ravishankar Shukla University, Raipur Chhattisgarh. Raipur is situated between 22˚ 33' N to 21˚ 14' N Latitude and 82˚ 6' to 81˚ 38' E Longitude. Urban site chosen as Raipur is the capital of Chhattisgarh and may be affected by the different type of particulate matter emitted from the variety of sources. Sampling site is 400 m away from the busy vehicular transport road and due to partial combustion of petrol, diesel, gasoline and biomass burning will be contributed high level of PM.

2. *Rural area (Rajim)*

Rajim sampling station (20˚ 59´ N 81˚ 55´E), located in Chhattisgarh, is believed to be a famous religious place due the confluence of three river (i.e. Mahanadi, Pairee and Sodbhadra) and is known as *Triveni Sangam*. The Rajim is about 45 km away from Raipur city. The sampling site

is situated at an altitude of 281 meter above sea level. The meteorological data, such as temperature, humidity, precipitation, wind direction and wind speed will be collected from Indira Gandhi Agricultural University Raipur, Chhattisgarh, India.

Both the study sites are entirely different in their emission characteristic properties, which will enable us for the suitable comparative study.

B. Aerosol sampling

1. Instruments to be used for sampling and their specifications

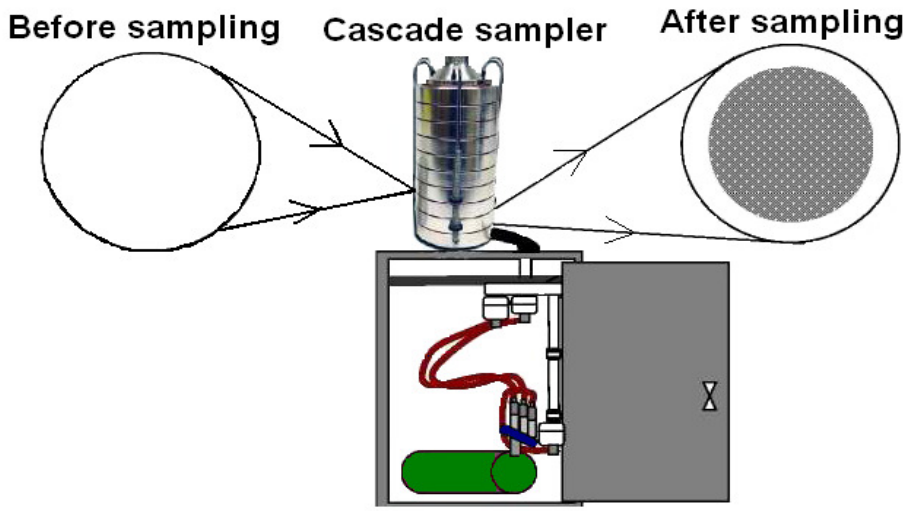
Sampler type	Model No.	Flow rate	
Anderson sampler	Modal TE 20−800 Tisch Air Pollution Monitoring Equipment USA	28.3 actual liter per min (ALPM)	
		Particle size	
		Stage	Cut off diameter, µm
		0	9.0-10
		1	5.8-9.0
		2	4.7-5.8
		3	3.3-4.7
		4	2.1-3.3
		5	1.1-2.1
		6	0.7-1.1
		7	0.4-0.7
		8	<0.4

2. Schedule for aerosol sampling

Sampling site	Sampling Month	No. of sampling in one month	Total sampling in one year	Total no. of samples in different particle size ranges				Total running time in single sampling, hr.
				PM_1	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}	
Urban area (Raipur)	12	4	48	48	48	48	48	48
Rural area (Rajim)	12	4	48	48	48	48	48	48

3. Sampling of aerosol

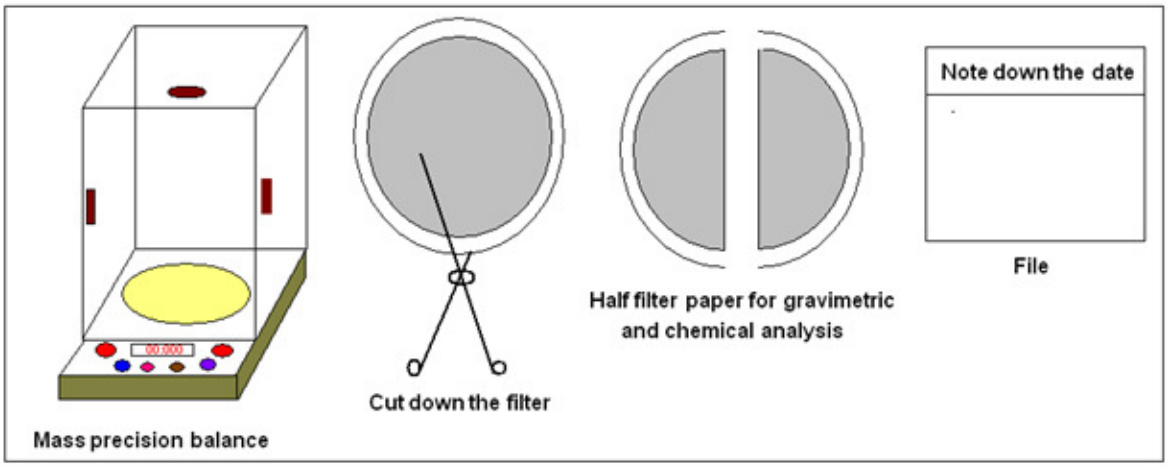
The collection of size-segregated aerosols will be performed at the terrace of a double-storied building in Raipur City, i.e. in Department of Chemistry of Pt. Ravishankar Shukla University at an altitude of approximately 15 meter above the ground level. Similarly, at Rajim sampling site, aerosol samples will be collected at the terrace of a double-storied building at an altitude of about 15 meters above the ground level. Ambient aerosol samples will be collected with Anderson sampler (TE 20–800, Tisch Air Pollution Monitoring Equipment, USA) for one year from July 2012 to June 2013 spread over all the major seasons, monsoon (June 15, 2012 to September), winter (October to January), spring (February to March) and summer (April to June 14, 2013). The sampling frequencies will nearly be two samplings per week starting at 06:00 hrs (local time) for 24 hrs. The flow rate of the Anderson sampler will be 28.3 L/min. The filters to be used in this study will be quartz fiber filters. Before use, the quartz fiber filters will be pre-backed at 550°C for about 15 hours to remove residual impurities. It may be noted that glass-microfibre filters may render positive artifacts by absorbing volatile compounds, resulting in overestimated gravimetric data, and concentrations of organics (Anhydrosugars and sugar alcohol) and ionic species (Yu *et al.*, 2006). PM of diameter less than 0.4 µm will be collected in backup filter installed in the final stage of cascade impactor. During the period of study 96 samplings (96 × 8 size fractions = 768 samples of eight different size fractions) will be carried out. PM_{10} particles will present the sum up of particles of stage 0 to stage 7 of the eight-stage cascade impactor. After the collection of aerosol samples, the eight-stage cascade impactor loaded with sampled filters will be transported from the sampling site to the laboratory. The filters will be unloaded in a dust free room and subsequently stored in Petri dishes and will be transported to the weighing room for gravimetric analysis.



C. Gravimetric analysis

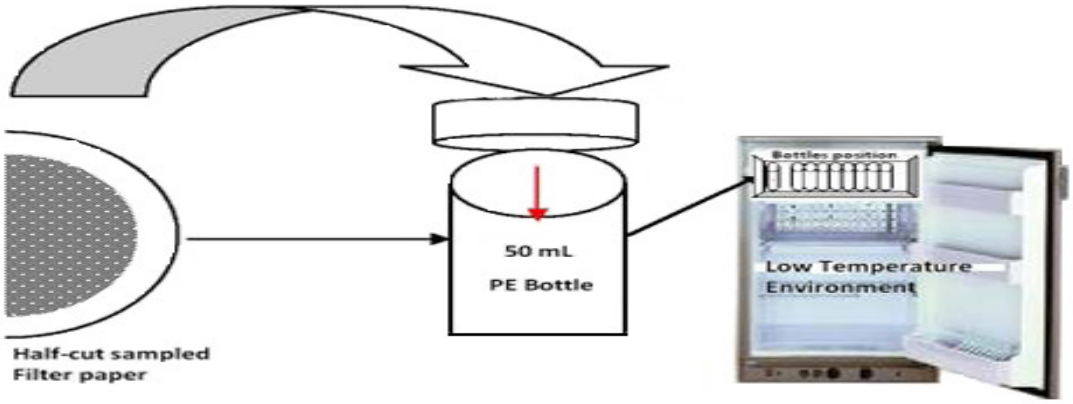
The mass concentration of size-segregated aerosols will be determined by the gravimetric analysis. The filters will be placed in desiccators for ~24 hrs before and after the sampling to remove the absorbed water and weighed in a controlled environment chamber, after taking the filters out of the desiccators, using an analytical balance (Sartorius, Model CP225D) with a reading precision of 10 µg. In this study, PM_{10} concentration will be calculated by summing the concentration of PM in all eight-size ranges (0.4 µm to 10µm) and backup filter, therefore, each of the filters will be analyzed gravimetrically by taking proper care in order to prevent minute deviation in weight measurements. Two of the most important factors to consider mass concentration measurement are variation of weight with temperature (T) and relative humidity (RH). Thus, the filters will be first conditioned for ~24 hrs at 20°C and 40% RH. All weight measurements will be repeated three times to ensure reliability. To ensure the quality of data, field blanks will be also collected.

The gravimetric mass (µg) will be calculated by subtracting the weight of the filter after sampling from that of the prior sampling and the concentration (µg/m^3) will be determined by dividing the aerosol mass by total volume of air sampled (m^3). After the gravimetric analysis, the loaded filters and field blanks will be placed in clean polyethylene (PE) bottles and stored in a refrigerator at about ~4°C to prevent the loss of volatile or semi-volatile species from the sample filters. The mass of the sampled filters obtained will be corrected for field blank values.


Note down the date
File
Half filter paper for gravimetric and chemical analysis
Cut down the filter
Mass precision balance

D. Preservation of aerosol sample

Aerosol samples are preserved in the low temperature environment. For this preservation filter is cut down into two pieces pack in small air tight bottle and stored it in freezer at ~4°C prior to analysis to prevent the loss of volatile species, especially anhydrosugars and sugar alcohols. Low temperature is an essential requirement for the storage of aerosol sample. After gravimetric analysis one-half of the filter will be packed in individual bottles and will be put in freezer.



E. Instrument to be used for chemical analysis and sample preparation

Anhydrosugars and sugar alcohol will be analyzed using ion chromatography (IC). The anhydrosugars levoglucosan (1,6-anhydro-b-D-glucopyranose CAS 498-07-7, 99.9% purity), mannosan (1,6-anhydro-b-Dmannopyranose, CAS 14168-65-1, >98% purity), and galactosan (1,6-anhydro-b-D-galactopyranose, CAS 644-76-8, 99.7% purity) will be obtained from Carbosynth (Berkshire, UK) and the sugar alcohols myo-inositol (>99%) and glycerol (>99.5%)

from Merck; xylitol (>99.5%) will be obtained from Calbiochem (Damstadt, Germany). One hundred mg of each compound will be dissolved in deionized water and the final volume will be adjusted to 100 mL for a 100 mg L^{-1} stock solution. These solutions will be stored at –18°C until used to make standard solutions and these, in turn, will be stored at ~4°C to prevent degradation during analysis.

Anhydrosugars and sugar alcohols will be determined in Taiwan by Prof. Y.I. Tsai, one of our research collaborators, using a Dionex ICS-2500 IC equipped with pulsed amperometric detection (PAD), a GP50 gradient pump coupled to a Teflon injection valve with 400–μL sample loop, a CarboPac MA1 guard column (50 mm length × 4 mm I.D.) and anion-exchange analytical column (250 mm length × 4 mm I.D.), a Dionex ED50 electrochemical detector with a gold working electrode and a pH electrode as reference, and using 200 to 600 (gradient) mMNaOH eluent at a flow rate of 0.4 mL min^{-1}. Dissolution of carbonate into NaOH can hinder the separation and to reduce the potential for this, exposure of NaOH solutions to atmospheric CO_2 will be minimized (Tsai *et al*., 2010).

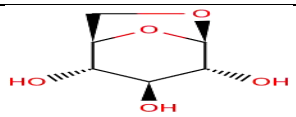
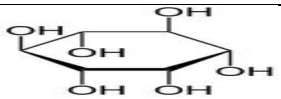
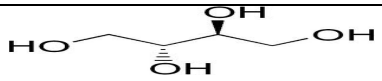
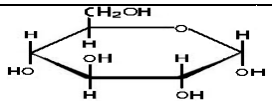
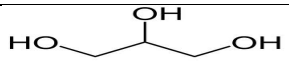
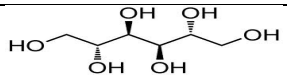
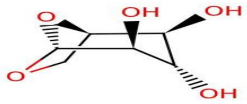
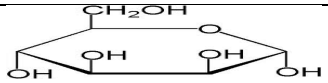
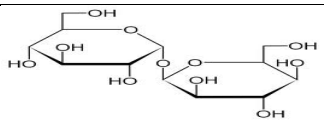
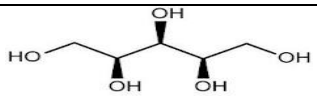
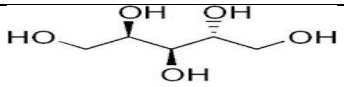
G. Studies on some important parameter

This study will provide data for PM concentration, size distribution between different particle sizes, and seasonal variation of anhydrosugars and sugar alcohols in the urban and rural area of Chhattisgarh, India.

Outcome of the present work

1. Present study will provide large data set of anhydrosugars and sugar alcohols content in size-segregated particulate matters in the urban and rural area of eastern central India.
2. This work will report the size distribution of anhydrosugars and sugar alcohols in particulate matter of eastern central India.
3. This study will enable us to estimate the contribution of regional biomass burning to global climate change.
4. This study will give data to examine the spatial and temporal evolution of atmospheric anhydrosugars and sugar alcohols.
5. Present study will provide sufficient data for comparative study to understand particulate characteristics; particularly, anhydrosugars and sugar alcohols in urban and rural area of central India.

List of anhydrosugars and sugar alcohols to be studied for chemical characterization

Species of interest	Chemical formula	Chemical Structure
Levoglucosan	$C_6H_{10}O_5$	
Galactosan	$C_6H_{10}O_5$	
Myo-inositol	$C_6H_{12}O_6$	
Erythritol	$C_4H_{10}O_4$	
Glucose	$C_6H_{12}O_6$	
Glycerol	$C_3H_8O_3$	
Mannitol	$C_6H_8(OH)_6$	
Mannopyranose	$C_6H_{12}O_6$	
Mannose	$C_6H_{12}O_6$	
Trehalose	$C_{12}H_{22}O_{11}$	
Xylitol	$C_5H_{12}O_5$	
Arabitol	$C_5H_{12}O_5$	

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